SCIENCE FOR CERAMIC PRODUCTION

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ANALYSIS OF SURFACE MICROSTRUCTURE AND QUALITY AND PROPERTIES OF ALUMINUM OXIDE SUBSTRATES

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A study is made of the surface quality of three types of corundum materials for microcircuit substrates. It is shown that after grinding and polishing the surface quality depends on the size of the crystals in the ceramic, which is determined largely by the particle-size of the initial powder and additions and the sintering regime.

Key words: corundum ceramic, polycore, KORAL-3, alumina, microstructure, size of crystals, surface purity, profilogram.

Ceramic has a number of unique physic-technical properties which virtually no class of materials possesses. High-strength ceramic materials obtained from oxides with regulator microstructure make it possible to fabricate new types of article with high-level properties for modern technology. Such materials have been developed on the basis of aluminum oxide, zirconium dioxide, their combined mixes, spinel, mullite, and others [1 – 3].

Compared with all other oxide materials, corundum ceramic is widely used in many areas of technology because of the collection of high-level physical-technical properties.

Diverse ceramic materials with high density, fine-crystalline structure, bending strength 300 – 800 MPa, excellent electric-insulation properties, high thermal conductivity, transparency to light, radiation resistance, and high chemical stability have been developed on the basis of corundum. These materials possess high hardness and durability and biological inertness and they can be used at temperatures to 1750 – 1800°C [4 – 7].

An important area of application of corundum ceramic is electronic technology. At the present time high requirements are imposed on substrates for microcircuits and correspondingly on materials for fabricating them.

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On account of its good electrophysical properties, high chemical characteristics, and highly pure surfaces corundum ceramic is now most widely used in electronic technology in the form of the most diverse articles, including substrates for integrated circuits.

The requirements imposed on corundum materials used as substrates are very stringent with respect to properties and especially surface roughness. The best materials are nonporous substrates with fine-crystal and uniform structure, which permit obtaining by grinding and polishing a surface of high purity and with low defect density. Such materials have high mechanical strength, maximum thermal conductivity, high insulation power, low dielectric losses, high resistance to high-temperature heating, and durability.

The most important quality of the characteristics of articles is minimum variance of the indicators of their properties and stability of the properties when in service. The indicators depend on the purity of the initial material, the porosity and microstructure of a ceramic, i.e. on the technological factors which must take account of all the fine points of the processes occurring in ceramic technology.

An important indicator, the microstructure, of a ceramic for substrates determines (provided that the structure has no pores and the initial materials are of high purity) all of the most important properties of articles. Ceramic microstructure depends on the structure of the initial powder, the type and distribution of the additive, the mechanism of sintering, and the firing regime. According to the published literature, the size of the crystals of the ceramic which is used for substrates ranges from 1 to 5 μm, i.e., the degree of recrystalli-

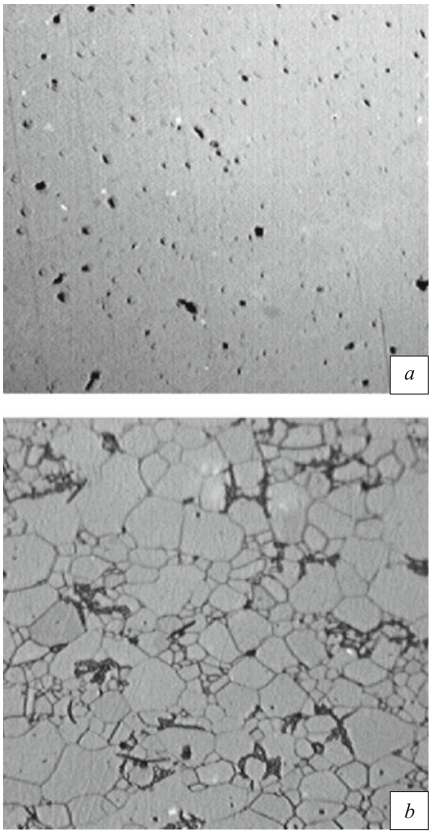

Fig. 1. Polished surface of a substrate consisting of “Polikor” ceramic (× 200): *a*) no etching; *b*) after etching.

zation during sintering is very low. For this reason, the main problem is to limit crystal growth as much as possible during firing. Aside from the size of crystals, the degree of intergrowth of crystals along boundaries, which occurs during sintering, strongly influences the degree of surface roughness during mechanical working of substrates. Crystal boundaries must have low angles and the optical properties of the boundaries must be identical to those of the rest of the crystal volume, i.e., the ceramic must have a monolithic structure whose optical properties are close to those of a single crystal. Such structure can be achieved with a definite mechanism of sintering, where in the process of removing porosity the crystals move under surface tension into the volume of the pores and turn until the crystal lattices coincide, inter-growing in the process. Such a structure gives high purity under surface grinding and prevents protrusions of crystals, since crystal bonds along boundaries are very strong.

The problem in developing new materials based on aluminum oxide for substrates of integrated circuits is to develop such a structure.

“Polikor” JSC is at the present time practically the only company fabricating substrates for microcircuits and a corundum-based material which can be used for producing small bases for resistances. First, G-0 alumina is ground with the additives boric acid and magnesium salt; this is followed by calcination at 1600°C and then wet grinding to obtain alumina G-0-P with adequate dispersion. This is the alumina, containing 0.3%[6] MgO, that “Polikor” JSC is now using to produce substrates by the method of casting film on a binder in the form of rubber dissolved in benzene. This permits distributing the binder uniformly over the volume of the mix and to obtain “Polikor” ceramic whose properties satisfy the requirements of ShchO781.000 TU for fabricating substrates.

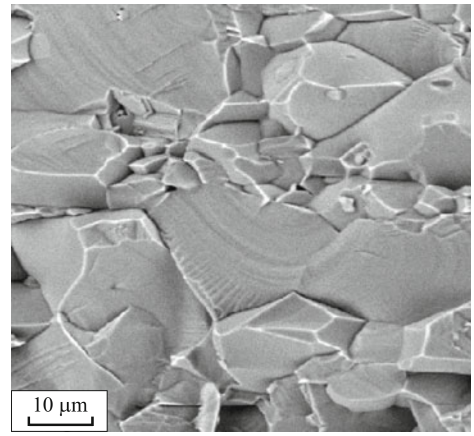

Fig. 2. Electronic photograph of the structure of “Polikor” ceramic (cleavage surface).

Basic Properties of “Polikor” Ceramic

Content, wt.%:	
Al_2O_3	99.7
MgO	0.3
Sintering temperature, °C	1750
Density, g/cm^3	3.96
Bending strength, MPa	≥ 280
Permittivity:	
at 10^6 Hz	≤ 10.8
at 10^9 Hz	≤ 10.0
Tangent of the angle of dielectric losses	$(1 - 2) \times 10^{-4}$

A polished surface of a substrate fabricated by “Polikor” is shown in Fig. 1.

The surface of the ceramic was etched at 1450°C in air for 1 h. The microstructure of the ceramic is nonuniformly crystalline; the size of the crystals covers a wide range — from 5 to 40 μm. Evidently, the magnesium oxide which is introduced and which must impede recrystallization is not completed uniformly distributed.

A photograph of the structure of the cleavage surface of the same substrate (Fig. 2) confirms the nonuniformity of the crystalline structure.

From the authors’ standpoint not only must the fabrication technology be improved but new compositions which would make it possible to obtain a completely new surface quality of the substrates meeting modern requirements must also be developed. Such possibilities certainly exist. Many

6 Here and below — content by weight.

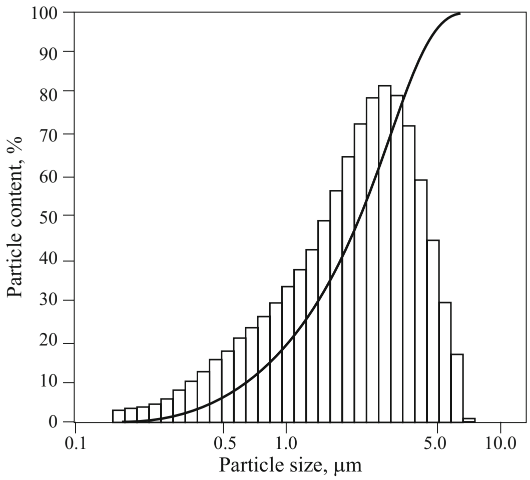

Fig. 3. Particle size distribution of G-0-P alumina, $S_{sp} = 0.8\ m^2/g$.

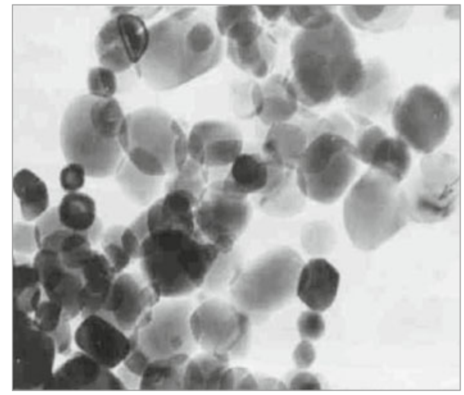

Fig. 4. Photograph of particles with the composition $Al_2O_3 - ZrO_2$.

studies of corundum materials with different additives of nanodisperse powders with different compositions attest to the possibility of obtaining nonporous materials which will make it possible to attain high-quality polished surfaces.

The present work gives the results of investigations of the fabrication of materials and substrates based on aluminum oxide used at “Polikor” with additions of $Al_2O_3 - ZrO_2$ nanopowders.

The particle-size distribution of alumina G-0-P used in “Polikor” JSC for fabricating substrates is shown in Fig. 3.

The main particle size of alumina is 1 – 5 μm. The introduction of 1% addition of nanopowder with the eutectic composition of the systems $Al_2O_3 - ZrO_2$ does not permit obtaining ceramic close to the nonporous state with such alumina dispersity. For this reason, 2% of the indicated additive was introduced into the G-0-P-based mix. KORAL-3 powder was obtained for fabricating KORAL-3 ceramic.

The added powder was made by heterophase chemical precipitation of hydroxides from a solution of concentrated salts of aluminum and zirconium. The hydroxides obtained were comminuted by the wet method in the presence of yttrium chloride, which with subsequent calcination partially stabilizes the zirconium dioxide.

In connection with their high dispersity the calcination temperature of the precipitated aluminum and zirconium hydroxides was ≤ 1350°C and the fired powder of the mix was comminuted for 24 h, which helped to decrease the particle size to 30 – 40 nm and the size of the aggregates to 100 – 200 nm (Fig. 4).

To develop a temperature – time regime for firing samples and an experimental batch of substrates, the sintering of samples from powder based on the mix developed was studied first.

The differential curve attests to sharp slowing of the rate of shrinkage at 1600°C. The samples from the mix developed, consisting of alumina with 0.3% MgO as an addition and 2% addition of $Al_2O_3 - ZrO_2$, were pressed into small 6 × 5 × 40 mm beams and 30 × 40 × 3 mm plates on a paraffin binder at pressure 100 MPa and fired in a vacuum furnace at 1680°C with preliminary soaking at 1580°C. Prior to firing the binder was burned out at 1400°C in air.

The KORAL-3 ceramic samples obtained were ground and polished at “Polikor” JSC, after which the quality of their and microstructure was evaluated. A photograph of the polished surface of a KORAL-3 ceramic plate is presented in Fig. 5*a*.

After polishing the surface of this ceramic differs substantially from the surface of the polished “Polikor” ceramic. Individual pores up 1 μm in size are present.

A photograph of the microstructure of the same sample after thermal etching at 1350°C in air for 1 h is presented in Fig. 5*b*.

The structure of the KORAL-3 ceramic differs sharply from that of “Polikor.” The main size of the crystals is 4 – 6 μm. The structure is quite uniform. But individual crystals up to 8 – 10 μm in size are present. A eutectic phase in the form of interlayers can be seen between the crystals; this phase ensures that the samples sinter by means of viscous flow and formation of coherent (intergrown) crystal boundaries (Fig. 6). Individual intracrystalline and intercrystalline pores up to 1 μm in size are present.

The surface roughness of the polished KORAL-3 ceramic consisted of depressions and asperities with depth and height, respectively, totaling 35 mm over length 100 μm.

Basic Properties of KORAL-3 Ceramic Samples

α-Al_2O_3 content, wt.%	99.1
Average grain size in the finished product, μm	To 5 – 6
Surface roughness, μm	0.01 – 0.04
Surface purity class	14
Thermal conductivity, W/(m · K)	32*
Permittivity at 1 MHz	9.6 ± 0.2*
Tangent of dielectric losses angle at 1 MHz	2×10^{-4}*
Density, g/cm^3	3.98
Bending strength, MPa	360 ± 20

* Data of Scientific – Research Institute of Measurement Systems, Nizhny Novgorod, Russia.

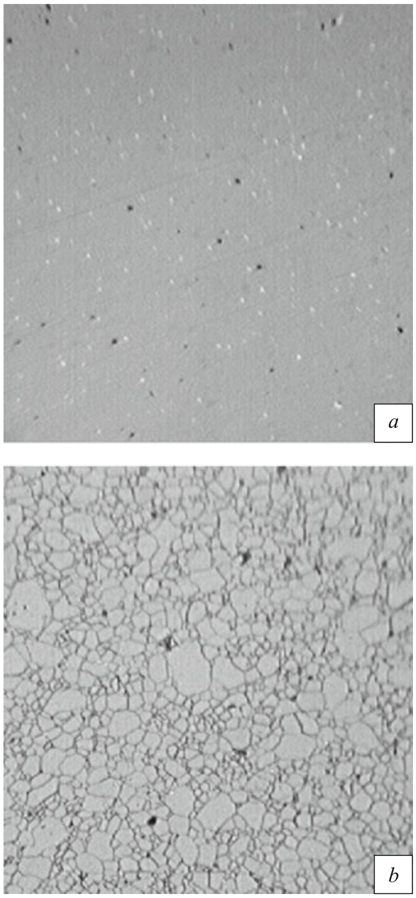

Fig. 5. Photograph of the microstructure of the polished surface of the ceramic KORAL-3 (× 200): *a*) no etching; *b*) after etching.

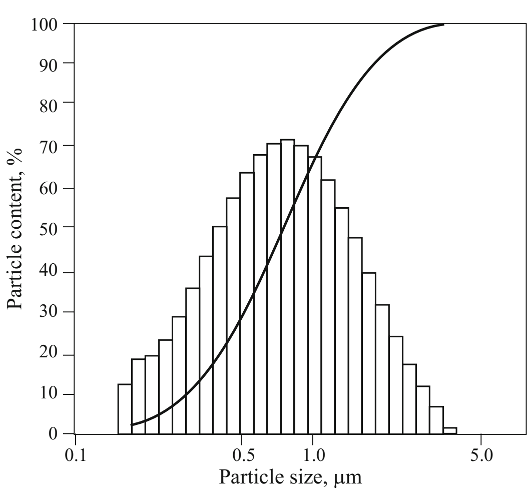

Fig. 6. Electronic photograph of the structure of the ceramic KORAL-3 (cleavage surface).

Aside from the KORAL-3 ceramic, the technology of obtaining high-density ceramic for CT3000SG alumina substrates manufactured by the German company Almatis was investigated. This alumina differs from the domestic alumina by its high purity and dispersity and can be used in the delivered state without preliminary preparation for fabricating high-density articles, which can be obtained by calcination in air at temperatures 1500 – 1550°C. The particle size distribution curve of this alumina is presented in Fig. 7.

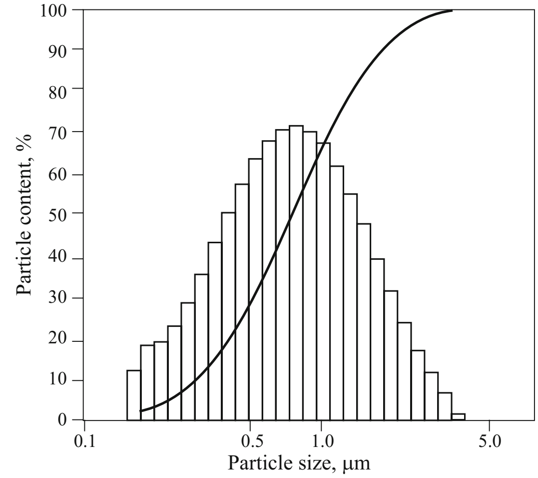

Fig. 7. Particle size distribution of alumina from the company Almatis, $S_{sp} = 7\ m^2/g$.

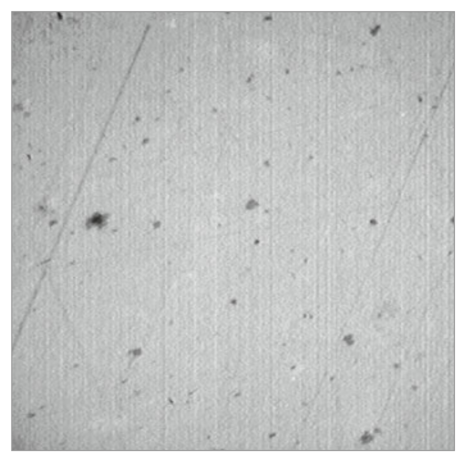

Fig. 8. Photograph of the microstructure of the polished surface of a sample of unground alumina from the company Almatis (× 200).

Alumina is characterized by high dispersity with average particle size 0.7 μm. However, quite detailed investigations have shown that substrates with high-quality surfaces cannot be obtained from such alumina. A high closed porosity (about 2%) always remains, and it makes it impossible to obtain high surface quality.

A photograph of the microstructure of a polished surface of a sample of plates fabricated from this alumina with no pre-preparation and sintered at 1550°C is shown in Fig. 8.

The ceramic is characterized by the presence about 2 μm pores.

When the polished samples were heat-treated at 1350°C in air the microstructure could not be discerned, probably because of the very fine crystalline structure. Photographs obtained in an electron microscope confirmed this (Fig. 9). The

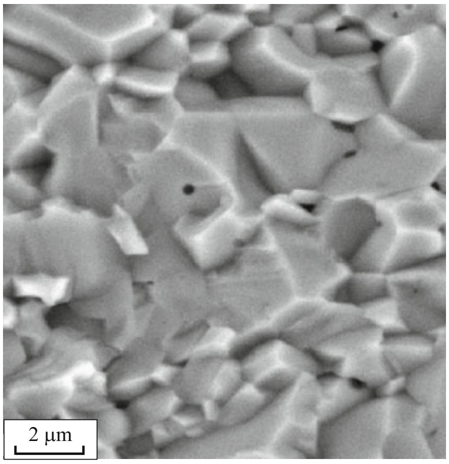

Fig. 9. Electronic photograph of the structure of a ceramic made from unground alumina from the company Almatis (cleavage surface).

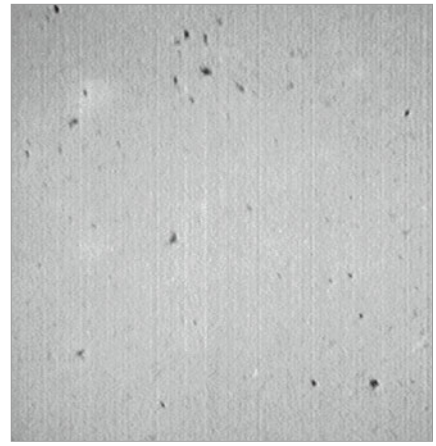

Fig. 11. Photograph of the microstructure of the polished surface of ceramic made from alumina calcined at 1200°C and comminuted over 24 h (× 200) from the company Almatis.

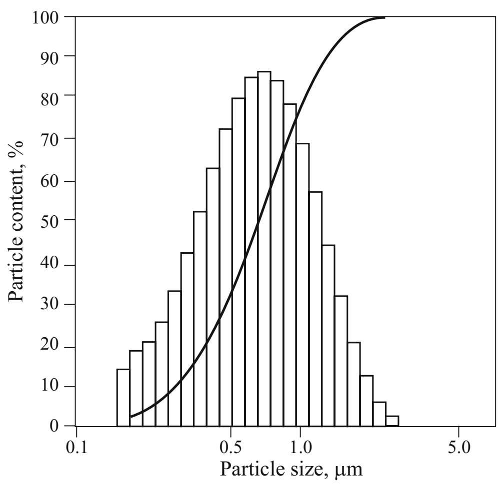

Fig. 10. Particle size distribution of alumina powder calcined at 1200°C and comminuted over 24 h alumina from the company Almatis, $S_{sp} = 12\ m^2/g$.

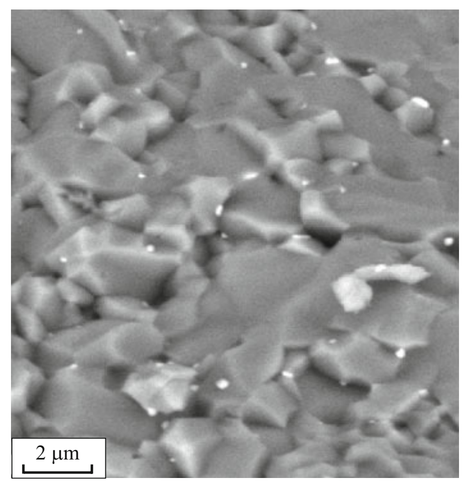

Fig. 12. Electronic photograph of the structure of a ceramic made of calcined and comminuted for 24 h alumina from the company Almatis (cleavage surface).

crystal sizes in the ceramic were 3 – 4 μm, but the presence of pores is observed.

The continuous shrinkage was determined. The differential curve characterizing the rate of shrinkage showed that on different temperature sections the sintering rate changes, which could be due to new growths that change the sintering process.

A more subtle investigation of the surface established that clusters of very fine pores are formed locally and sintering does not completely remove them.

The authors assumed that alumina is modified by optical additions, to preserve its sintering activity. However, these modifications, which burnup during sintering, rupture the micro-volumes in the samples, from which pore are not removed.

For this reason a decision was made to first calcinate the initial alumina at 1200°C in air in order to remove the presumed modifiers and then to wet comminute for 24 h to ensure its sintering activity.

The particle-size distribution of the powder of German ground alumina from the Almatis company is presented in Fig. 10.

The maximum particle size of the alumina decreases, and the average particle size also decreases — to 0.6 μm.

The continuous shrinkage with a differential curve showing the rate of shrinkage versus temperature was determined for samples of this alumina. The curve does not contain any oscillations of the sintering rate; shrinkage completion shifts in the direction of decreasing temperature. The temperature – time sintering regime of the substrates made of the comminuted alumina from the Almatis Company was determined on the basis of the shrinkage. Figure 11 shows a photograph of the microstructure of the polished surface of a plate made of this alumina.

The surface of the plates is pure with single pores substantially smaller than 1 μm. The fine-crystalline structure of the ceramic made it impossible to etch the surface thermally. Figure 12 shows an electronic photograph of the microstructure of this ceramic, which is characterized by crystals with sizes 2 – 3 μm and the virtual absence of pores.

The surface obtained was distinguished by the lowest roughness compared with all other materials. The roughness of the polished surface of a ceramic sample made of CT3000SG alumina calcined at 2400°C and comminuted for 24 h was 25 nm, representing the sum of the depression depths and asperity heights, respectively, on length 100 μm.

Properties of Ceramic Samples Made from Alumina from the German Company Almatis, Calcined at 1200°C, and Comminuted for 24 h

α-Al_2O_3 content, wt.%	99.7
Average grain size in the finished product, μm	2 – 3
Surface roughness, μm	< 0.03
Surface purity class	14
Thermal conductivity, W/(m · K)	25 – 30*
Permittivity at 1 MHz	10.8*
Tangent of dielectric losses angle at 1 MHz	3.5×10^{-4}*
Density, g/cm^3	3.92
Bending strength, MPa	350 ± 20

* Data of Scientific – Research Institute of Measurement Systems, Nizhny Novgorod, Russia.

CONCLUSIONS

The investigations of the microstructure, surface quality, and properties of three types of corundum materials — Polikor, KORAL-3, and ceramic based on Almatis alumina — convincingly show that it is possible to fabricate high-quality substrates for microstructure from, first and foremost, domestic materials. One such material is KORAL-3, which is fabricated from alumina obtained in "Polikor" JSC for substrates with added nano-powder of a eutectic in the system $Al_2O_3 - ZrO_2$. The alumina from the German company Almatis is also very promising; the technology for obtaining substrates from this material can be successfully adopted at the enterprise "Polikor."

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